California Environmental Protection Agency

Air Resources Board

SOP MLD 031

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF PM10 TOTAL CARBON IN AMBIENT AIR

Northern Laboratory Branch
Monitoring and Laboratory Division

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1.0 SCOPE

This document describes a procedure for determining the total carbon content of particulate matter in the ambient air by the analysis of PM_{10} quartz-fiber filters. This procedure was developed by NLB staff.

2.0 SUMMARY OF METHOD

Atmospheric suspended particulate matter is collected over a 24-hour period on a 8 x 10 inch quartz-fiber filter. The filter is aspirated with a size selective inlet high volume sampler. A #2 cork borer is used to punch circular pieces from the exposed filter. Four filter punches are placed into the platinum sampling boat through a flip-top hatch on the Dohrmann carbon analyzer. The sample boat is subsequently advanced through a pyrolysis tube which contains a packed section of cobalt oxide (CoO). The pyrolysis tube is maintained at 800 °C and is continually flushed with ultrapure oxygen at 200 cc/min throughout the analysis. The sample is vaporized and swept into the packed section of the pyrolysis tube where the carbonaceous matter on the filter is oxidized to CO_2, H_20, SOx, NOx, etc. The oxidized gases are then scrubbed to remove corrosive species formed and the resulting CO_2 is carried into a linearized Non-Dispersive Infrared (NDIR) detector. The Electronics Module integrates the detector signal and displays the analysis result in parts per million carbon (ppmC) concentration units.

3.0 INTERFERENCES AND LIMITATIONS

3.1 Linearity for the instrument has been established within the range of 0 - 2200 ppmC. If the sample concentration exceeds the range of linearity, then an appropriate dilution must be prepared prior to subsequent analysis.

3.2 Results are directly affected by variances in the flow rate of ultrapure oxygen. Therefore, a flow rate of 200 cc/min ±20 cc/min must be maintained throughout the analysis day. The rate of flow is continually monitored by a flow meter, with LED readout, placed downstream from the NDIR.

3.3 Avoid the use of materials or solvents that contain carbon which may contaminate the system. Use non-carbon sampling media such as QMA

quartz-fiber filters.

3.4 Avoid exposure of nitric or sulfuric acid to the system. Each will contaminate the scrubber and interfere with results.

3.5 The Cu/Sn materials within the scrubber should be replaced monthly. Failure to do so may contribute to inconsistent background and results.

3.6 A single punch of blank quartz-fiber filter contains13 ppm carbon. This background level must be subtracted from all ambient samples.

3.7 Hamilton syringes used to deliver the standard solutions have reported accuracy and mechanical reproducibility specifications of ± 1% of the total volume.

3.8 If the background level of the detector varies by more than 10% from one day to the next, the detector cells should be cleaned of dust, water vapor, and corrosive gases.

3.9 Calibration of the instrument should be performed for each day before samples are analyzed.

3.10 A temperature variance exists within the combustion zone due to the space between heating elements in which the thermocouple rests.

3.11 A tartaric acid solution is used to standardize the analysis. It is assumed that all forms of carbon (inorganic, organic, and elemental) encountered in ambient samples are completely pyrolyzed/oxidized during analysis.

3.12 The detector module will display a ready signal with a readout of **<**0.0500. If the background signal of the detector exceeds this value, the detector zero potentiometer should be adjusted to a suitable (0.0100) operating level.

3.13 The cobalt oxide (CoO) catalyst located in the combustion zone will degrade over time thus contributing to inconsistent results. The catalyst, therefore, should be replaced on a regular (monthly) basis.

4.0 APPARATUS

4.1 Dohrmann model DC-85A High Temperature Total Organic Carbon Analyzer equipped with Boat Sampling Module, Non-Dispersive Infrared Detection Module, and Electronics Module.

4.2 Porter Instruments 4-channel LED display with 0-1000 sccm flow meter.

4.3 Porter Instruments model CMD-122 controller with model 201FSCV mass

flow controller.

4.4 Hamilton 50ul Gastight syringe.

4.5 Number 2 brass cork borer, 4.58 mm diameter.

4.6 Permeation dryer, Rosemount Analytical model 090-825.

4.7 Aluminum sheet, 10" x 14" x 1/8".

5.0 REAGENTS

5.1 Ultrapure grade oxygen.

5.2 Ultrapure grade nitrogen.

5.3 A 2000 ug/ml tartaric acid custom grade carbon standard from Inorganic Ventures.

5.4 A 2000 ug/ml tartaric acid custom grade second source carbon standard from Inorganic Ventures.

5.5 Baker Analyzed copper, granular 20-30 mesh, chemically pure. Tin, granular 30 mesh, certified A.C.S. grade.

5.6 Phosphoric acid, reagent grade, A.C.S. certified.

6.0 PROCEDURE

6.1 Instrument start up/shut down

6.1.1 Increase the pressure regulator attached to the ultrapure oxygen to approximately 30 psi.

6.1.2 Visually inspect the tin/copper scrubber to be free of water or other contamination. Verify that the sparger disperser is well submerged with acidified water (pH 2-3). Verify that the mist trap is less than ½ filled with water.

6.1.3 Set the mass flow controller (channel 1) to 38.1 (Display should then read 38.0).

6.1.4 Turn on permeation dryer gas (nitrogen) to 18 psi and then insert the free end of the teflon line which exits the sparger into the end of the combustion tube.

6.1.5 Change the mist trap.

6.1.6 Remove the sampling boat from the pushrod assembly. Scrape any residual quartz wool from the inside of the boat and then rinse with DI water. Replace with a new piece of quartz wool and use tweezers to carefully tamp down the wool.

6.1.7 Replace the sampling boat into the pushrod assembly, close the hatch cover and bake the sampling boat and wool until the baseline response returns to its original value.

6.1.8 Allow the system to equilibrate for 15 minutes.

6.1.9 For system shutdown, prior steps are reversed. First, remove Teflon tubing from end of combustion tube. Next, turn off gas to permeation dryer. Reduce flow though O_2 regulator to <10 psi and then set mass flow controller to 0.00.

NOTE: For further information on instrument set-up or parameters, consult the DC-85A systems manual (sections 4 and 5).

6.2 Instrument Calibration, Set-up and Analysis

6.2.1 The instrument must be calibrated using 2000 ug/ml tartaric acid carbon standard prior to each day's ambient analyses. The control standard and a check standard should be analyzed immediately after calibration. A check standard is then analyzed after every ninth sample run.

6.2.2 All liquid standards should be loaded into the Hamilton syringe and subsequently dispensed into the sample boat using the same technique. Rinse the syringe with nanopure water three times, then deliver 40 ul of standard solution into the syringe.

6.2.3 Remove the septa from the liquid injection port and carefully dispense the solution into the sample boat as not to splash any solution outside the boat. Replace the septa and wait exactly one minute prior to starting the analysis. Simultaneously depress the green instrument start button and begin to introduce the sample boat into the pyrolysis tube at a rate of approximately 1cm/sec.

6.2.4 After completion of two standard runs that are within 10 ppmC of each other, momentarily depress the yellow calibrate button located on the front panel of the instrument to update the calibration factor.

6.2.5 Repeat step 6.2.3 for injection of the control standard and check standard.

6.2.6 Obtain appropriate quartz-fiber PM10 filters from the extraction laboratory. See User Appendix I, LIMS Operations.

6.2.7 Enter sample information and results into the total carbon logbook.

6.2.8 Remove the piece of filter that contains stamped numbers on one edge and place the piece exposed side up onto the clean, dry, 10" x 14" sheet of aluminum. If the filter is complete and folded in half, the entire filter is then place onto the aluminum sheet but only punch out 1/4 of the filter containing the stamped filter ID.

6.2.9 Use the #2 cork borer and randomly remove 12 sample punches from the filter. Carefully lift the filter from the aluminum sheet as not to disturb any filter punches and replace it into the glassine envelope. Insert four sample punches into the sample boat through the flip-top hatch using tweezers and then close the hatch. Wait exactly two minutes for the background level to return to its original value and then simultaneously depress the start switch and begin to introduce the sample into the pyrolysis tube at a rate of approximately 1cm/sec.

6.2.10 When the analysis has been completed (4-8 minutes), the ready light will illuminate and a beep will sound. Record the results into the total carbon logbook. Remove the old sample punches from the boat and allow the assembly to cool for 30 seconds before continuing with the next sample.

6.2.11 Repeat the analysis procedure for a total of three analyses per filter with readings within 50 ppmC of each other.

7.0 QUALITY CONTROL

7.1 Duplicate analyses are performed for ten percent of all ambient samples received from the field. The relative percent difference (%RD) of the duplicate analyses is tabulated and is included in the quarterly quality control report.

7.2 The daily control standard is analyzed on a daily basis immediately following the calibration. The control standard must be within the control limits. Warning and control limits are established from historical data to track analytical trends. The warning limits are defined as ± two times the method standard deviation and the control limits are defined as ± three times the method standard deviation.

7.3 Standard checks should be analyzed following every ninth sample analysis in order to maintain a control on the instrument background and to check the validity of ambient sample results.

7.4 Due to the small size of each individual filter punch and due to the inhomogeneity present in ambient samples, each analysis consists of four punches and is analyzed in triplicate. This method of analysis seems to provide a good representative average of the carbon content of the entire quartz-fiber filter.

USER APPENDIX I
LIMS OPERATIONS

The ARB Laboratory Information Management System (LIMS) database is used to assist in the retrieval of ambient samples from the filter storage area, to automatically dictate which samples analyses are to be duplicated, and to enter analysis results for future data retrieval and reporting. The following is a general outline of the procedures that are commonly used in the analysis and data reporting of total carbon results.

1. WORKLIST GENERATION AND SAMPLE RETRIEVAL

1.1 Open the LIMS Reports icon.

1.2 Click on file then on run.

1.3 Select the y-drive, reports, and pmwrktc.rep.

1.4 Run report to the printer to obtain a print out of the samples that need the total carbon analysis.

1.5 From the printed total carbon worklist, the PM10 filters are obtained from the filter storage area and analyzed in the order shown on the worklist. Duplicate analyses should be performed on all samples that are designated by a 02 in the replicate (Rep) column of the worklist.

2. SAMPLE RESULTS ENTRY TO LIMS SYSTEM

2.1 Open Procomm-4, click on telnet, and then SQL*LIMS.

2.2 Enter username and password to log on to LIMS.

2.3 Type in user sample ID (or scan bar code).

2.4 Press enter and then the home key.

2.5 Page down to the total carbon (TC) data entry section.

2.6 Type in the analysis date and the three replicate TC values (TC-1, TC-2, and TC-3), respectively.

2.7 Press execute and enter to update the values.

2.8 Then record the PM10 total carbon result into the total carbon lab notebook.